LA-UR-21-22645
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Title:	Structured Membrane-electrode Interface for Highly Efficient PEM Fuel Cell
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Intended for:	Interview presentation
Issued:	2021-03-17

Structured Membrane-electrode Interface for Highly Efficient PEM Fuel Cell

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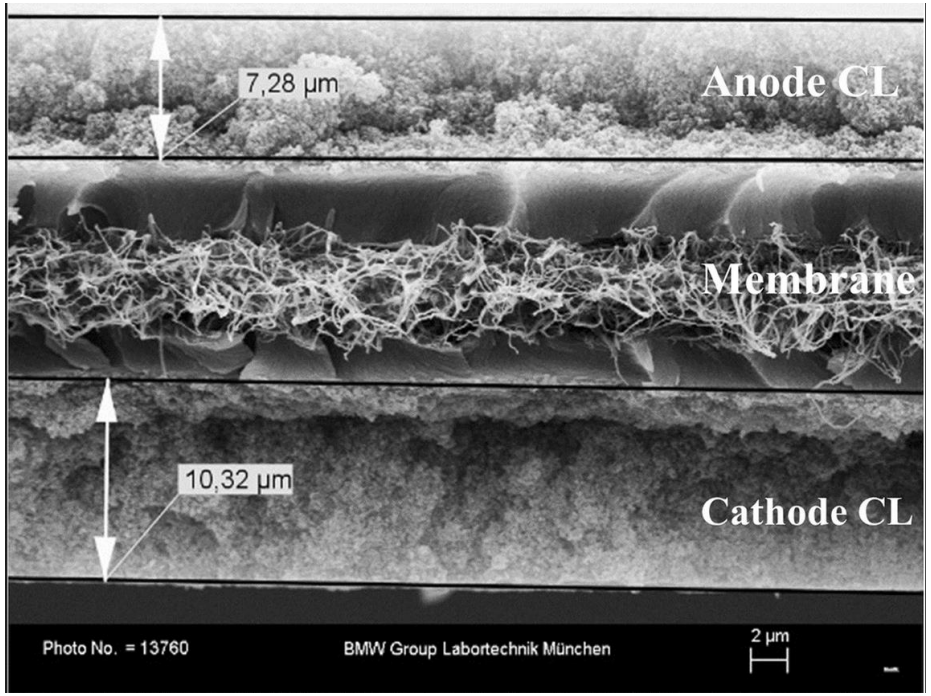
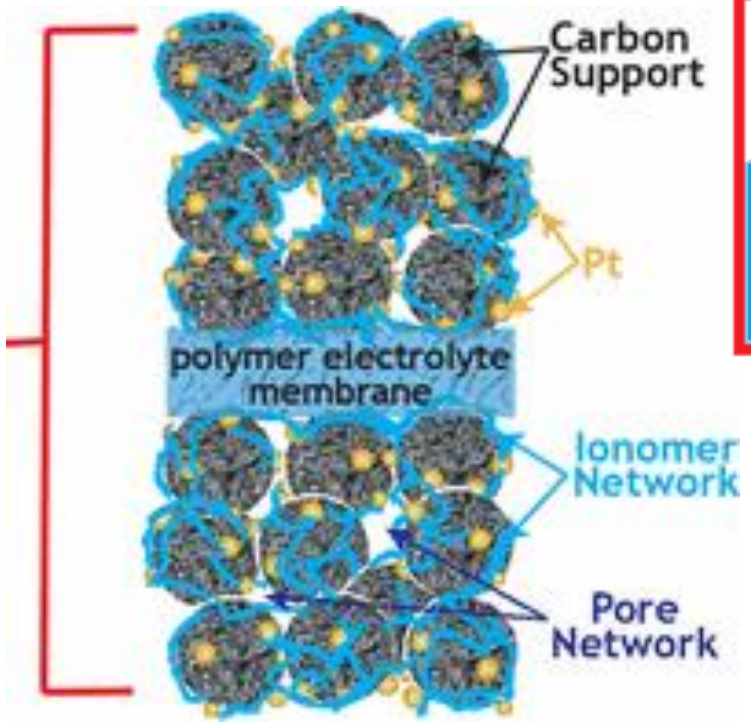
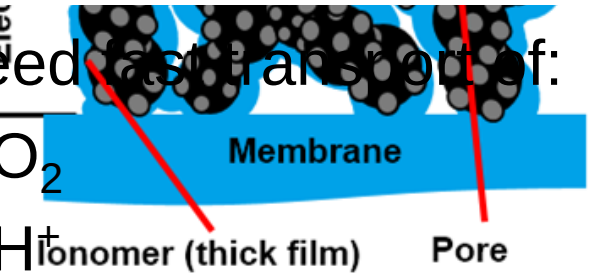
Conventional Electrode for PEM Fuel Cell







- Random mixture of:
  - Pt on C support (catalyst)
  - Ion-conducting polymer (ionomer)
  - Void space (pore)

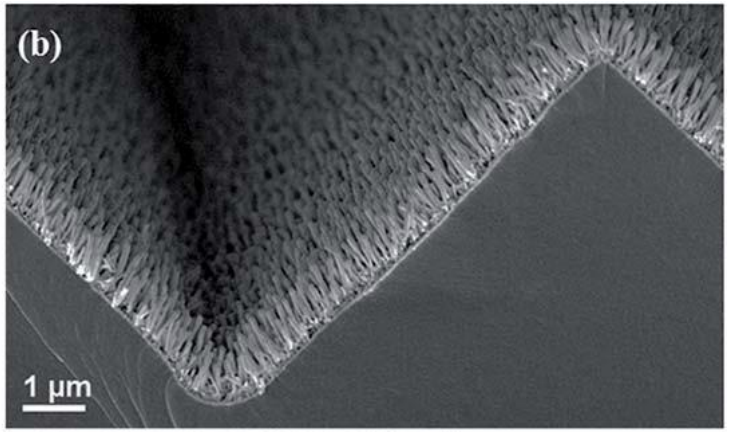
- Problem:
  - Thick catalyst layer
  - Long proton/electron transport pathway
  - High mass transport resistance
  - Low mass activity

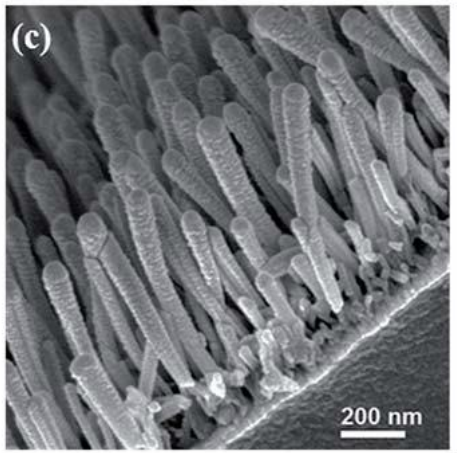
Need fast transport of:

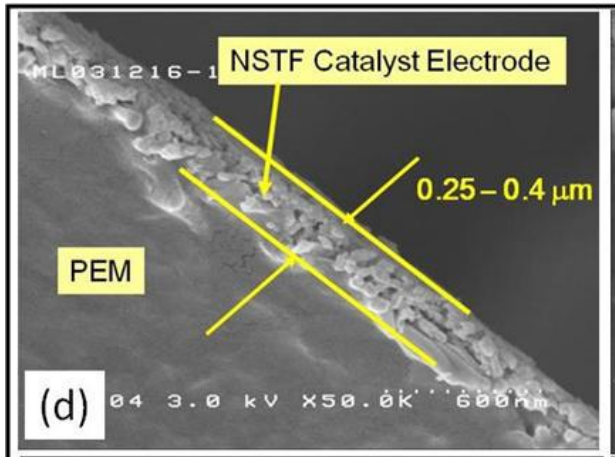
- O_2
- H^+
- e^-
- H_2O

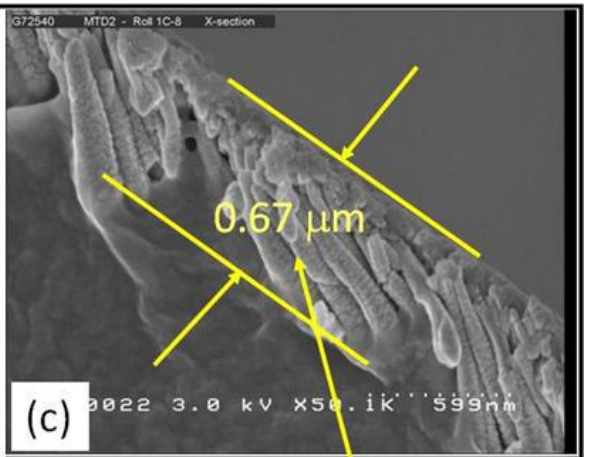
1. Sassin, Megan B., et al. *Anal. Chem.* (2017): 511-518
2. Obermaier, M. et.al . *Scientific reports*, *8*(1), 1-9.

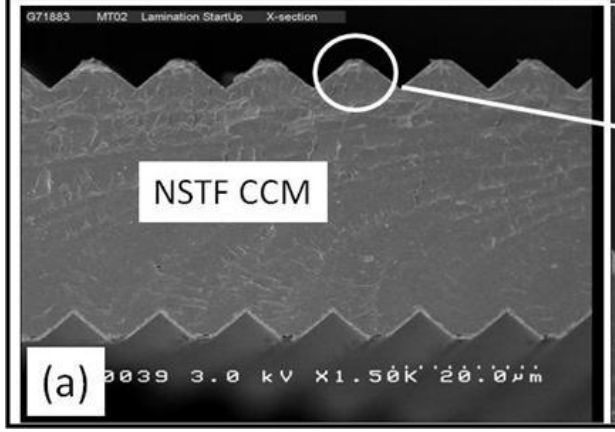
Prior Work: NSTF

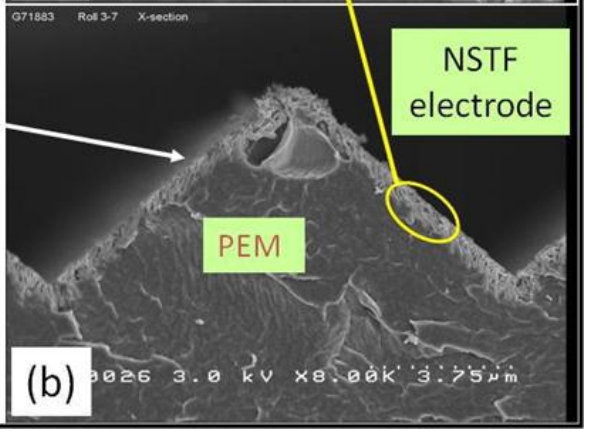












Cullen, David A., et al. *Journal of Materials Chemistry A* 3.21 (2015): 11660-11667.

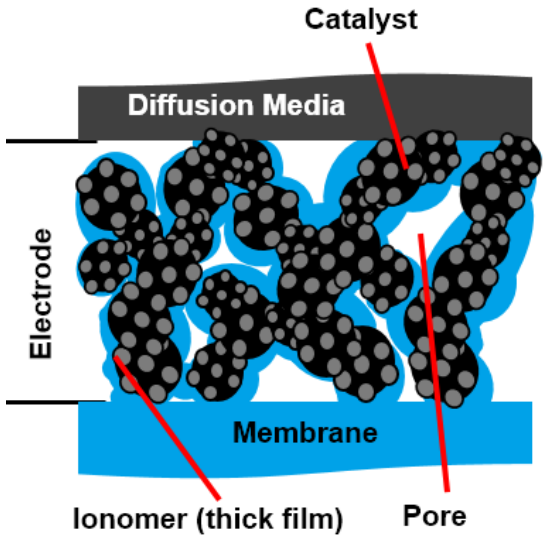
Debe, Mark K. *Ecs Transactions* 45.2 (2012): 47-68.

- Whiskers are significantly compressed and deformed, lead to mass transport problem
- Whiskers are compressed into the Nafion membrane, lead to reduction on active reaction sites.
- Limited proton conductive paths in the nano pt-coated whiskers compared to ionomer-containing electrodes.

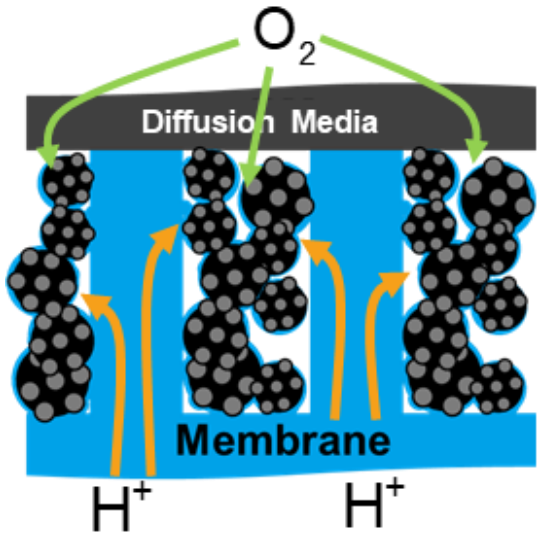
・Arrayed membrane with Pillars

Approach - Ordered Electrode

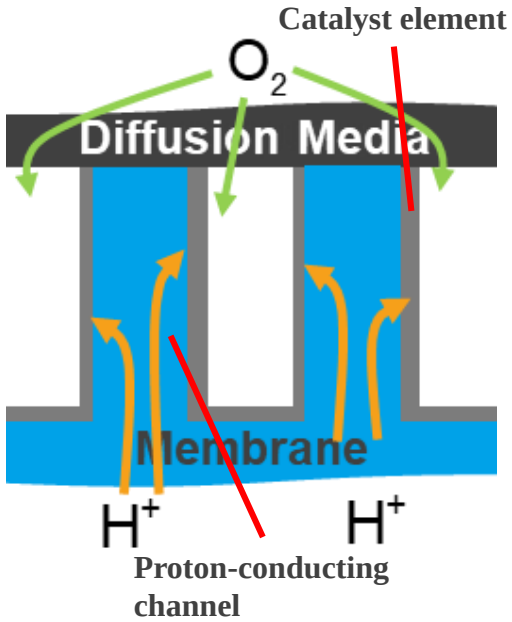
Conventional Electrode*



Array Electrode*



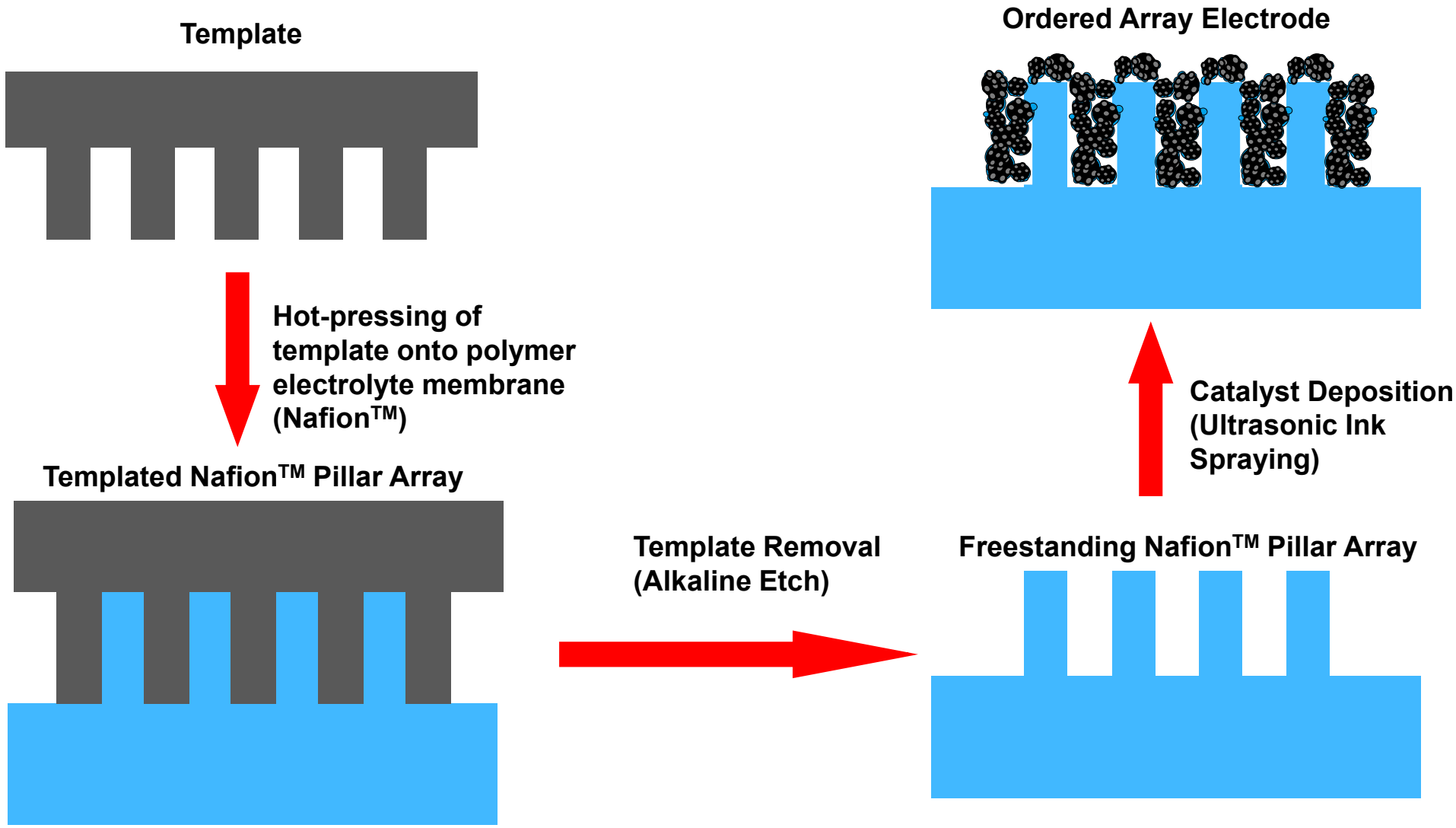
Nanowire Electrode*



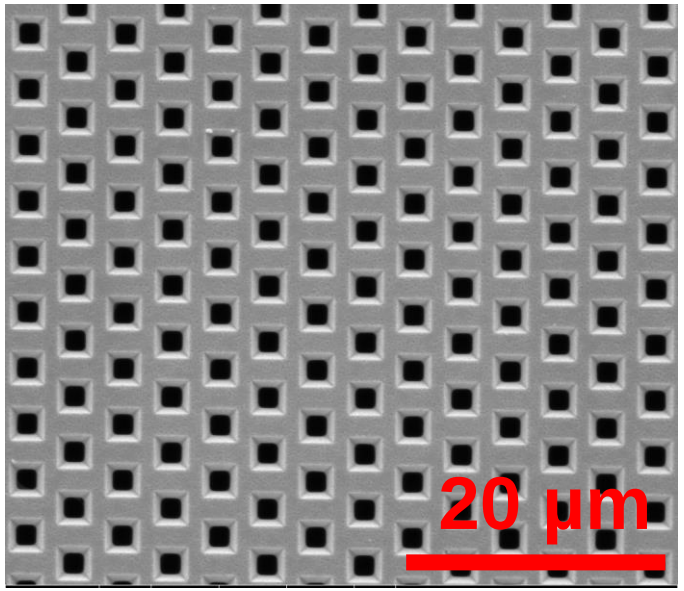
- Meso-structured electrode relies on vertically-aligned ionomer channels for long-distance H+ transport and catalyst support
- Catalyzed elements can have reduced ionomer content

*not to scale

Fabrication Process of Ordered Array Electrode



Fabrication Process of the Ordered Array Electrode

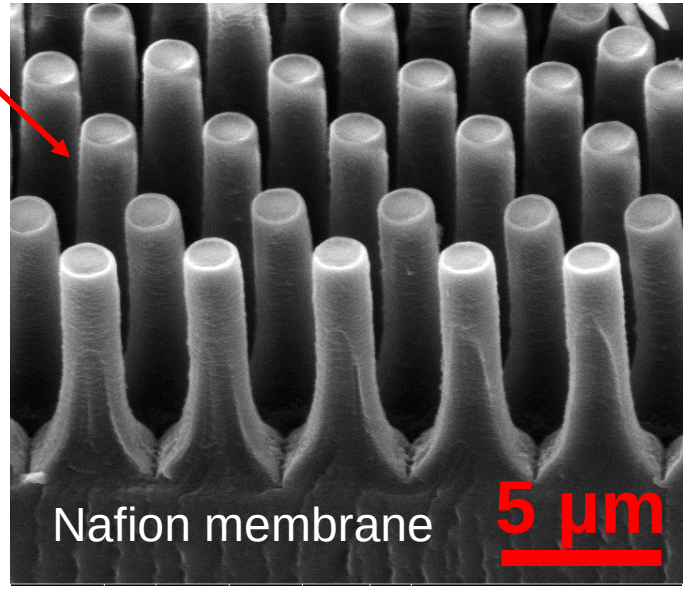


Si template

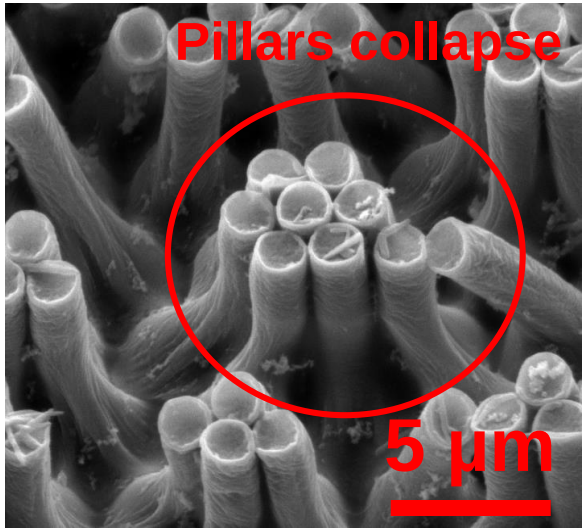
Hot-press with PEM

Dissolving template

Nafion
Arrayed
pillars



Catalyst deposition

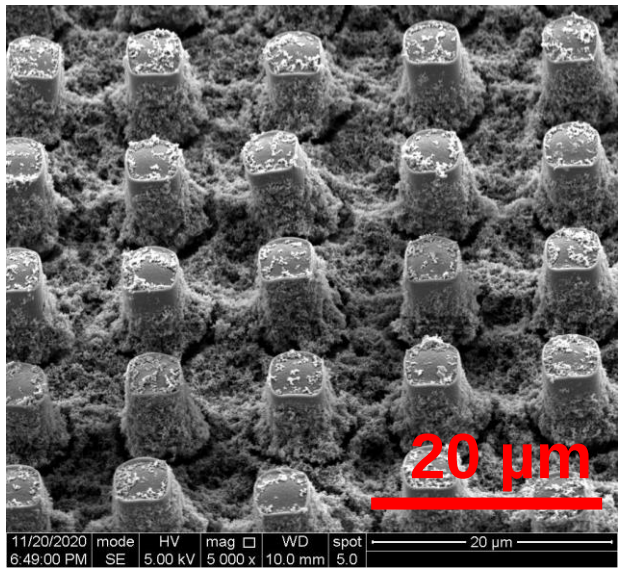


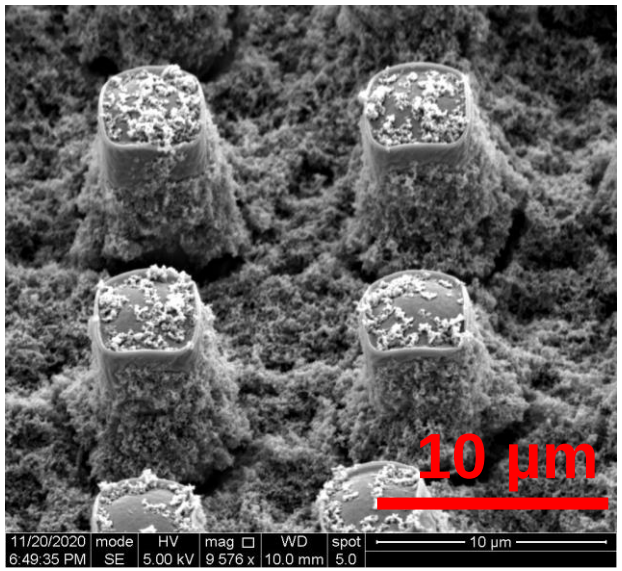
Pillar collapse during catalyst deposition.

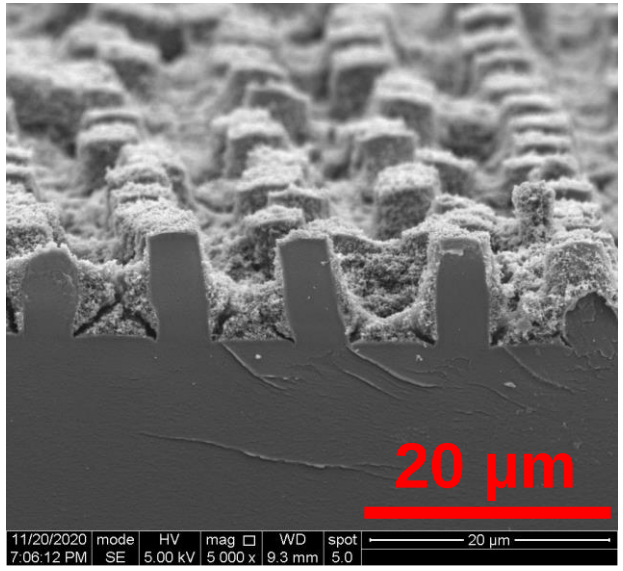
Preventing Nafion pillar collapse

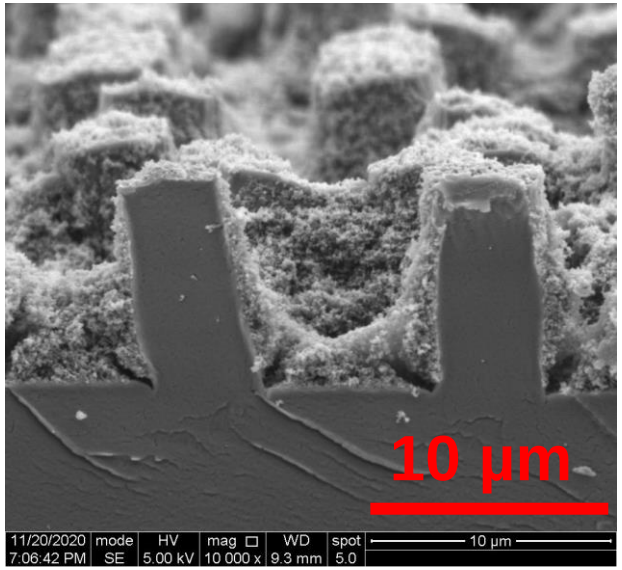
- Methods:
  - Different forms (H^+, Na^+, K^+)
  - Templates with different features
  - Different coating methods
  - Different deposition parameters
- Pillar length: 10 µm
- Spray coating:
  - Ink flow rate: 0.02 ml/min (ultralow)
  - Gas flow rate: 0.4 ml/min
  - High nozzle-sample distance: 60 cm

Accomplishment #1: Development of a robust method for catalyst deposition with prevention of pillar collapse.





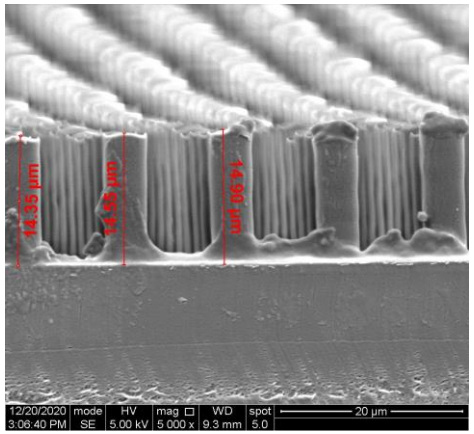


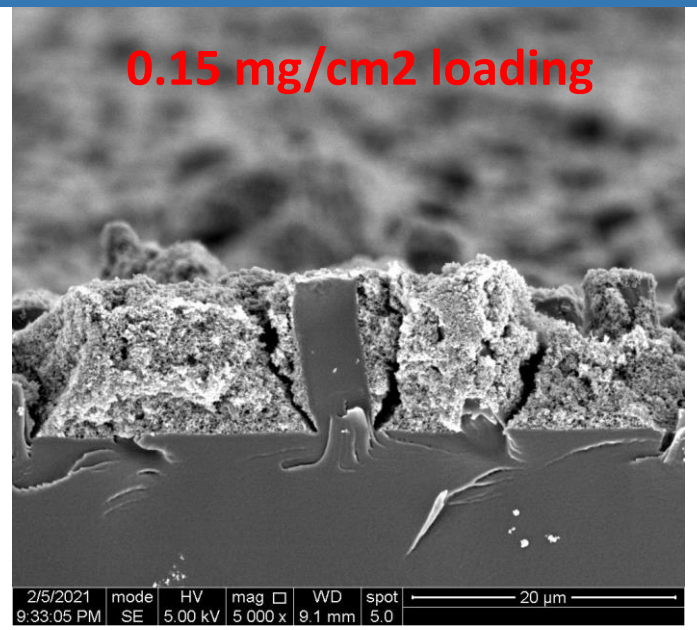


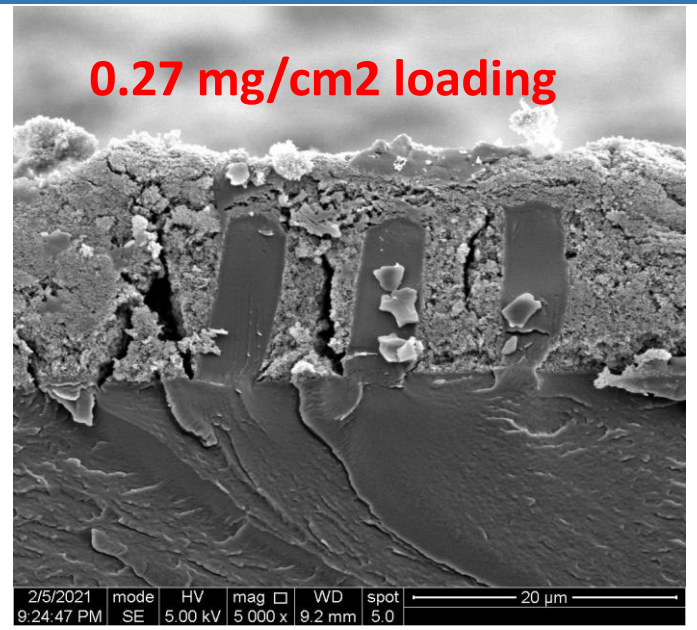
Regular pillar: 15 um for 0.3 mg/cm^2 loading

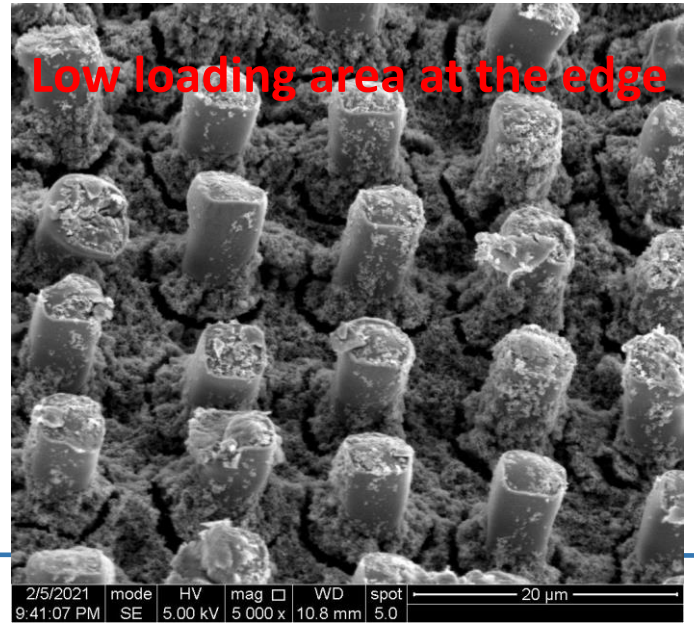
- Optimized spraying
- Pillar diameter: 5 um
- Pillar length: 15 um
- Relatively good structure with catalyst

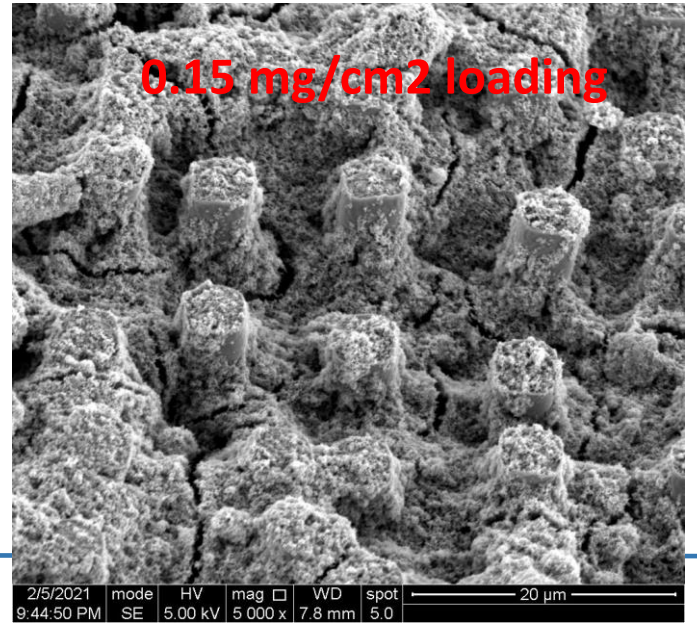
15-um-height pillar

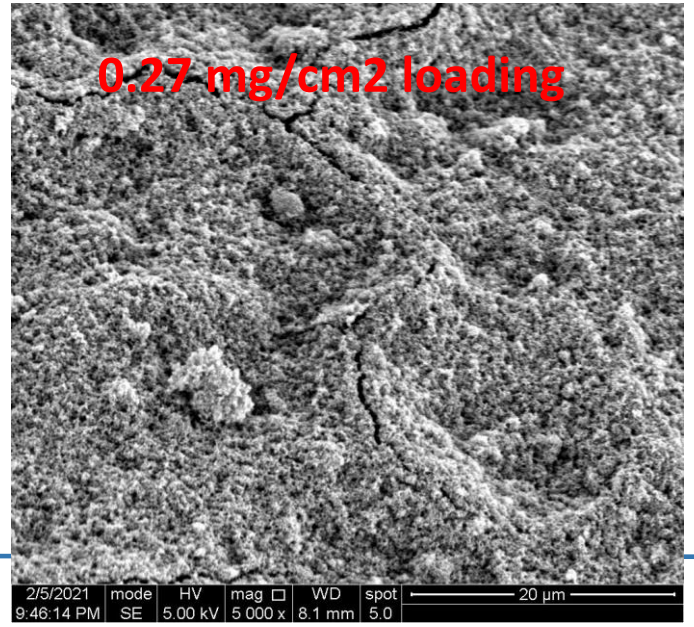






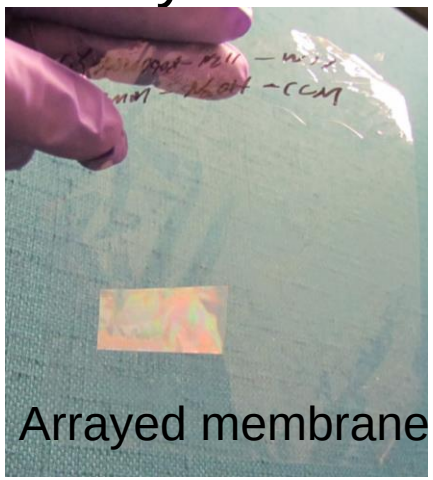


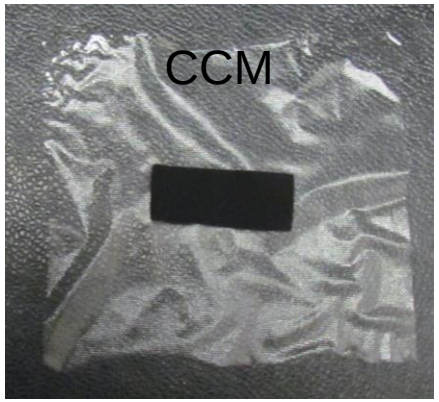


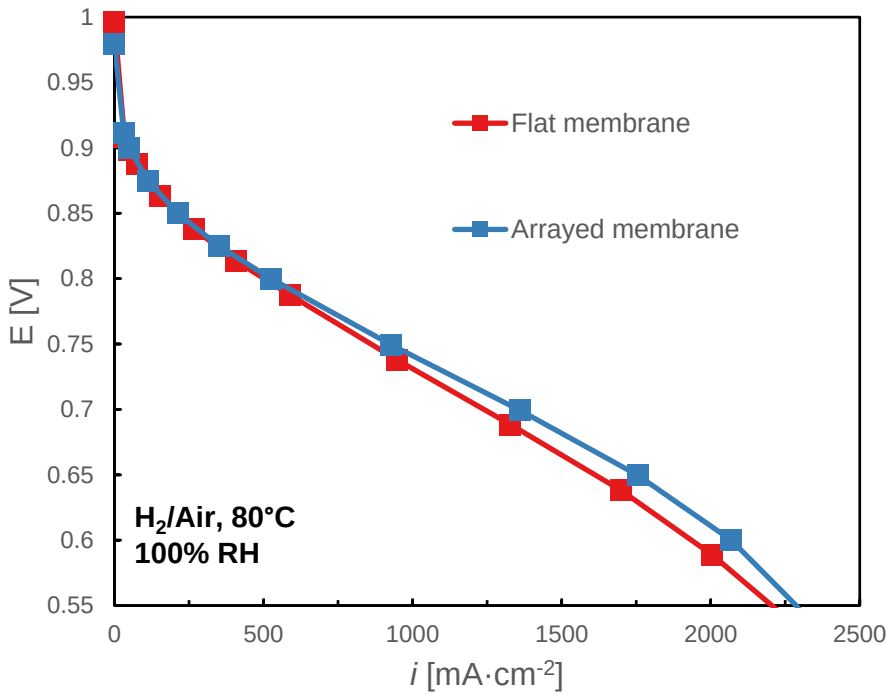


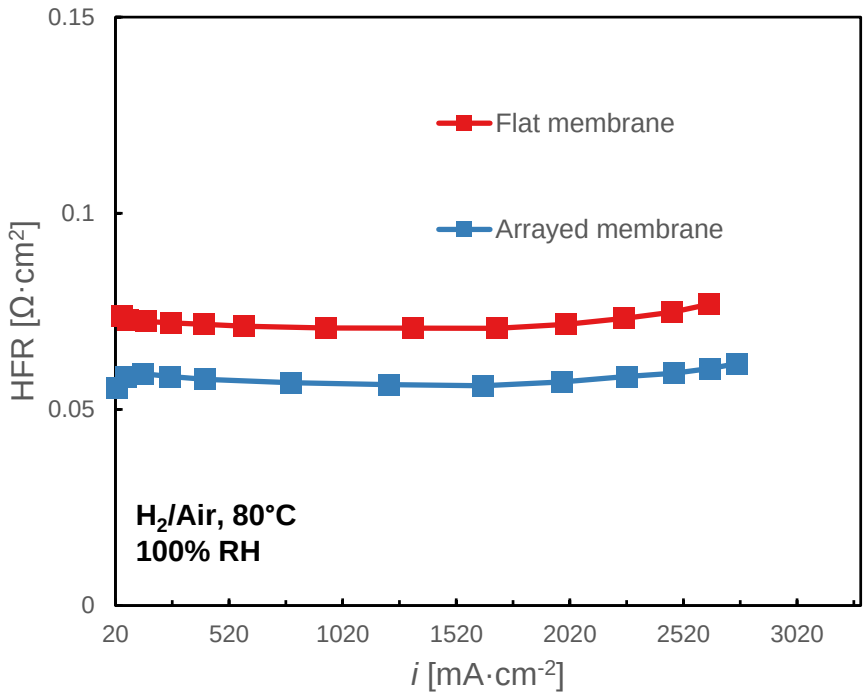
Arrayed membrane in Fuel Cell Test

- Arrayed membrane provide a better performance compared to flat membrane
- Patterned membrane provide a smaller HFR, due to the reduced Nafion content in catalyst ink and increased proton transport paths in Nafion pillars.





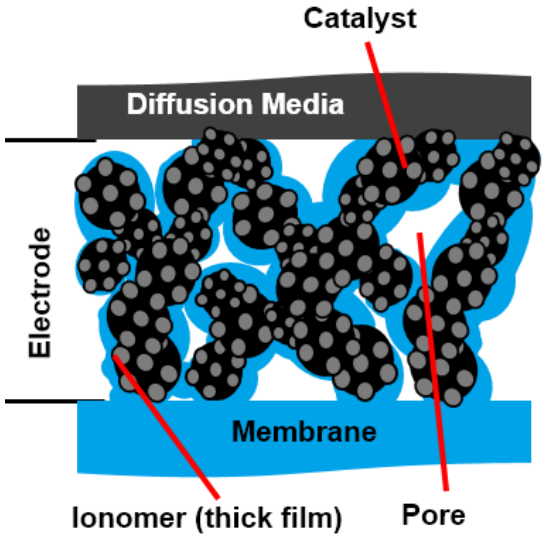




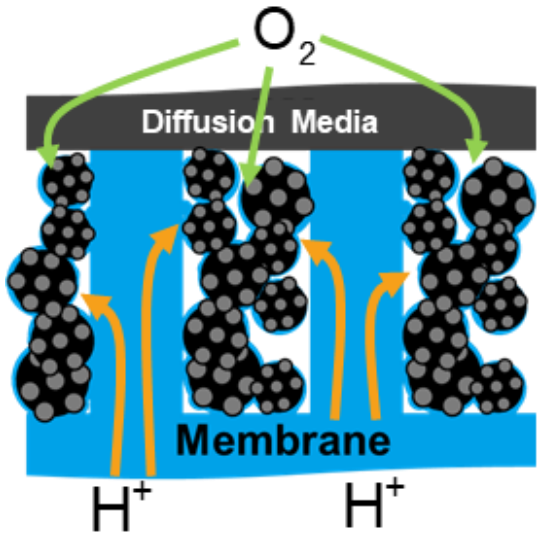
25 µm membrane; H_2/Air; Cell temperature: 80 ºC; 150 kPa

Co-axial Nanowire Electrode

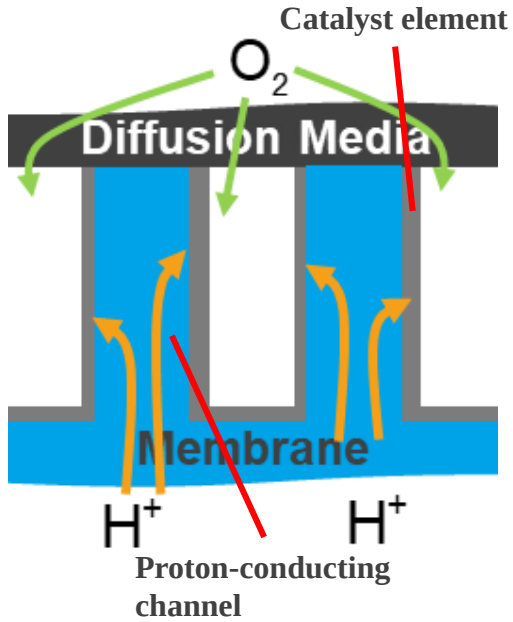
Conventional Electrode*



Array Electrode*



Co-axial Nanowire Electrode*



- CANE relies on vertically-aligned ionomer channels for long-distance H^+ transport and catalyst support
- Electrode with thin Pt film has reduced ionomer/carbon content

*not to scale

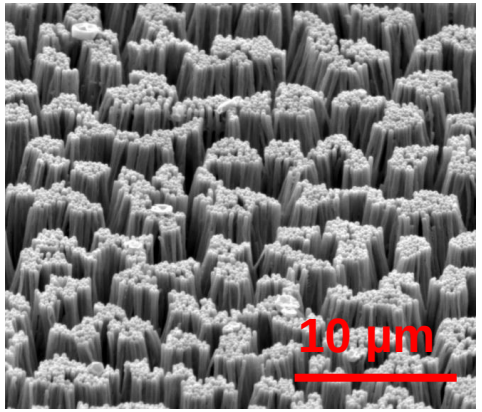
Fabrication Of Co-Axial Nanowire Electrodes

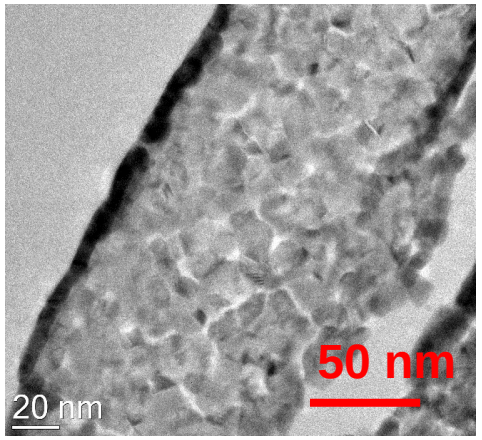
Anode Aluminum Oxide (AAO) Template

Atomic Layer Deposition of Pt Film

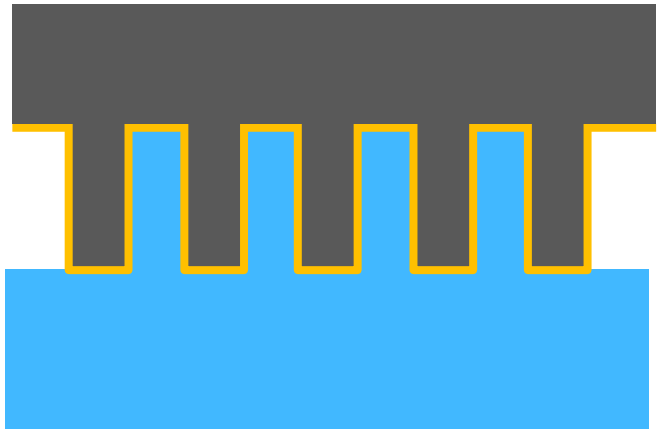
AAO Template with Pt

High roughness and high aspect ratio (5-25) utilized

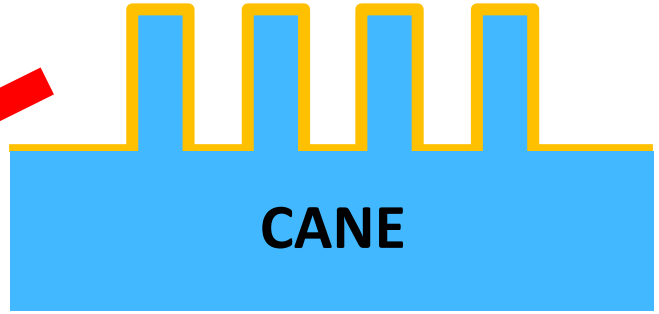




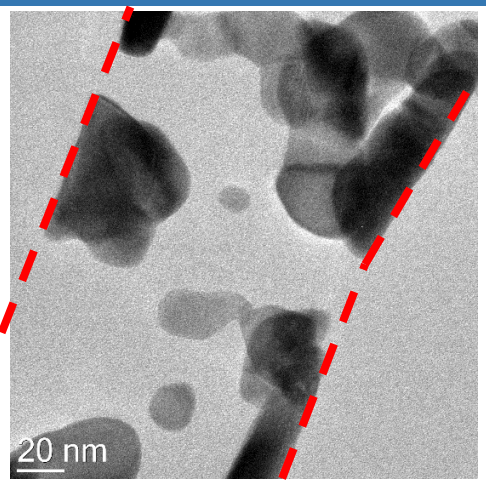
Hot-pressing of platinized template onto Nafion membrane



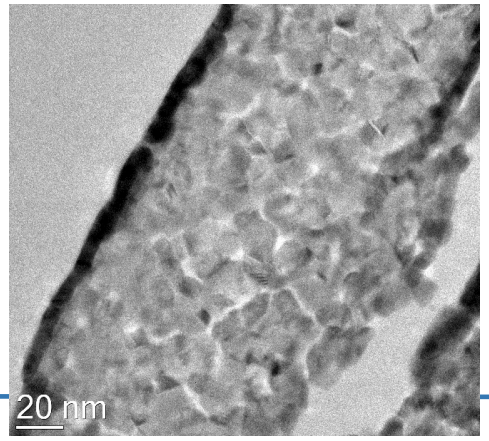
Template Removal (Acid Etch)

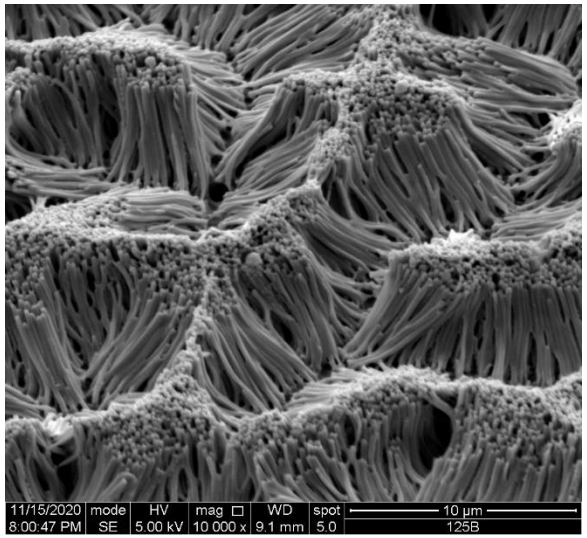


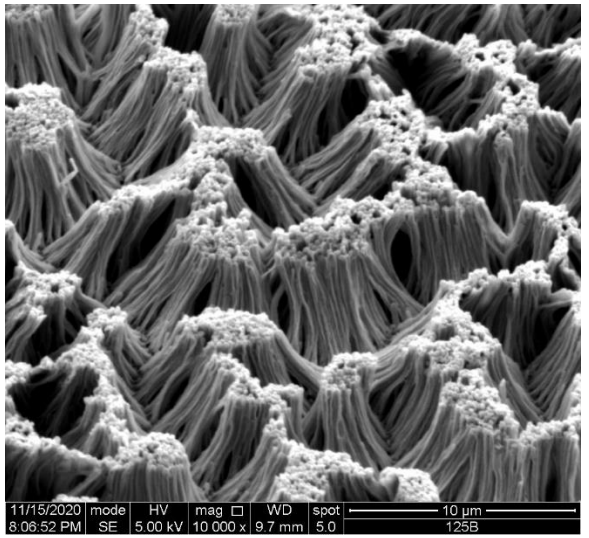
Co-Axial Nanowire Electrodes

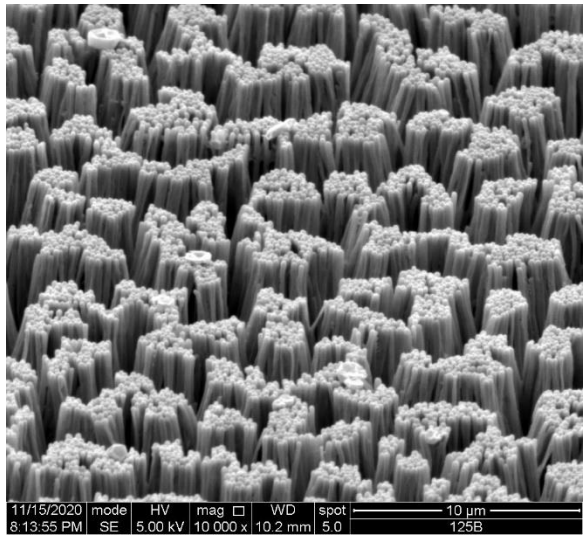


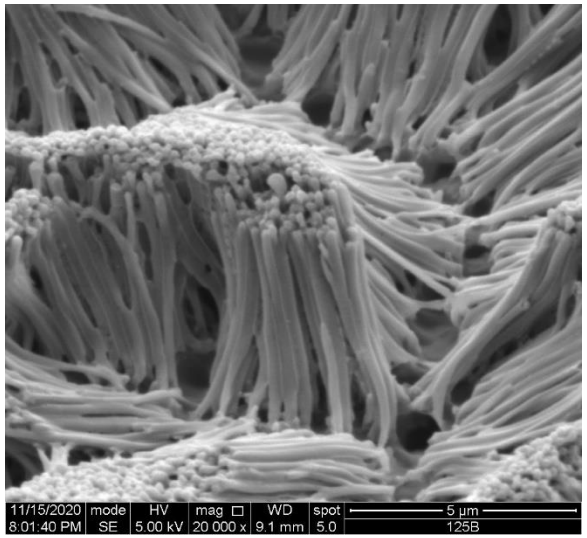
- Thicker Pt nanolayer leads to vertical pillars



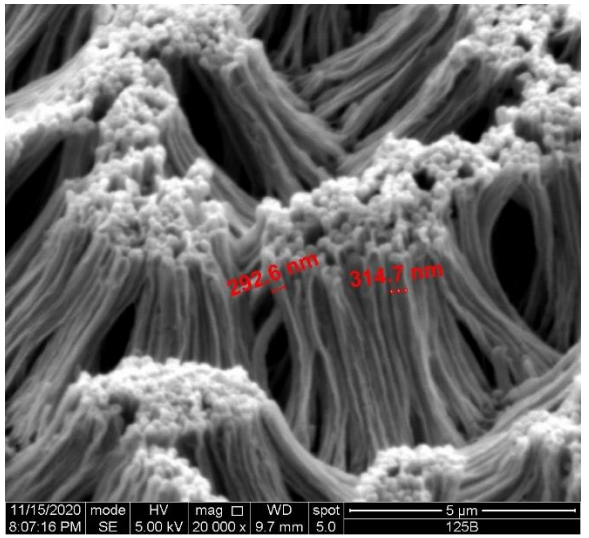




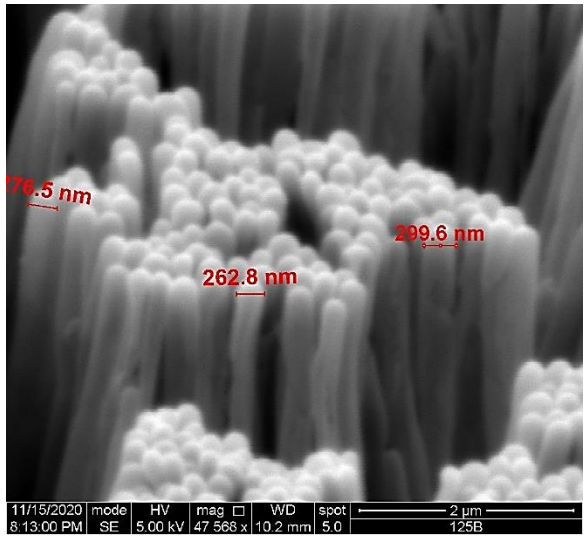




5um/2.5nm

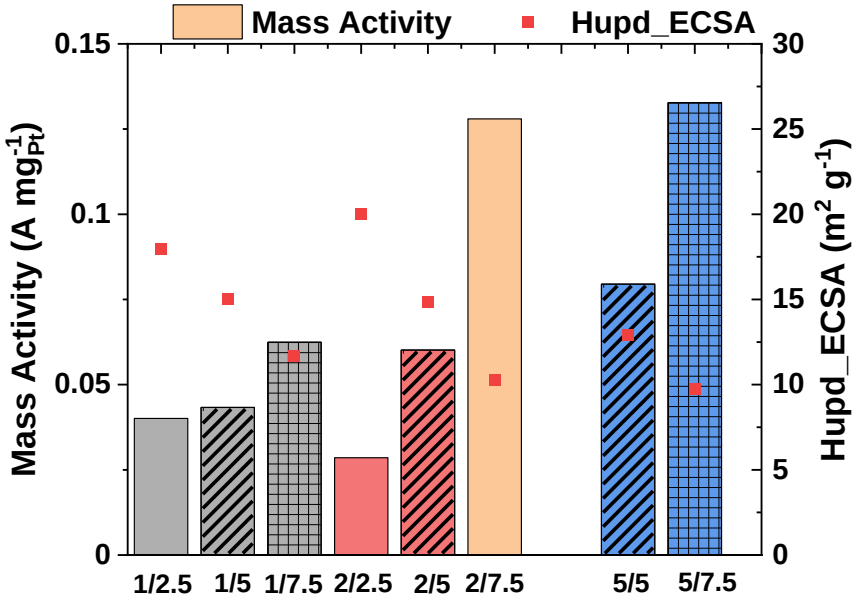


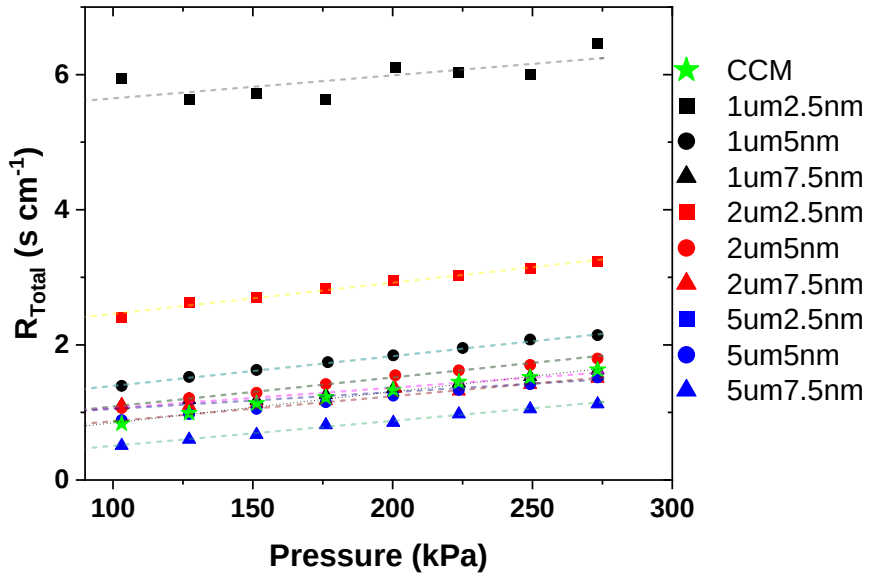
5um/5nm

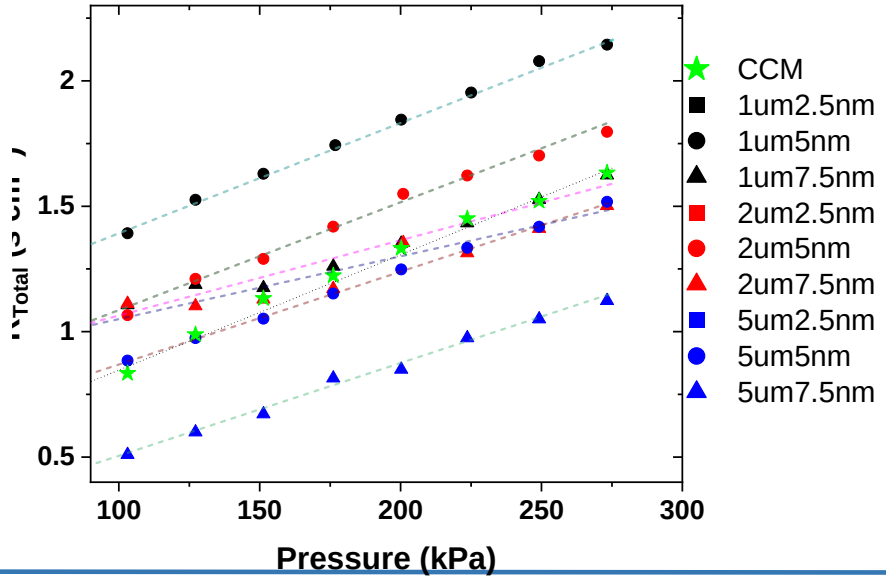


5um/7.5nm

Co-Axial Nanowire Electrodes

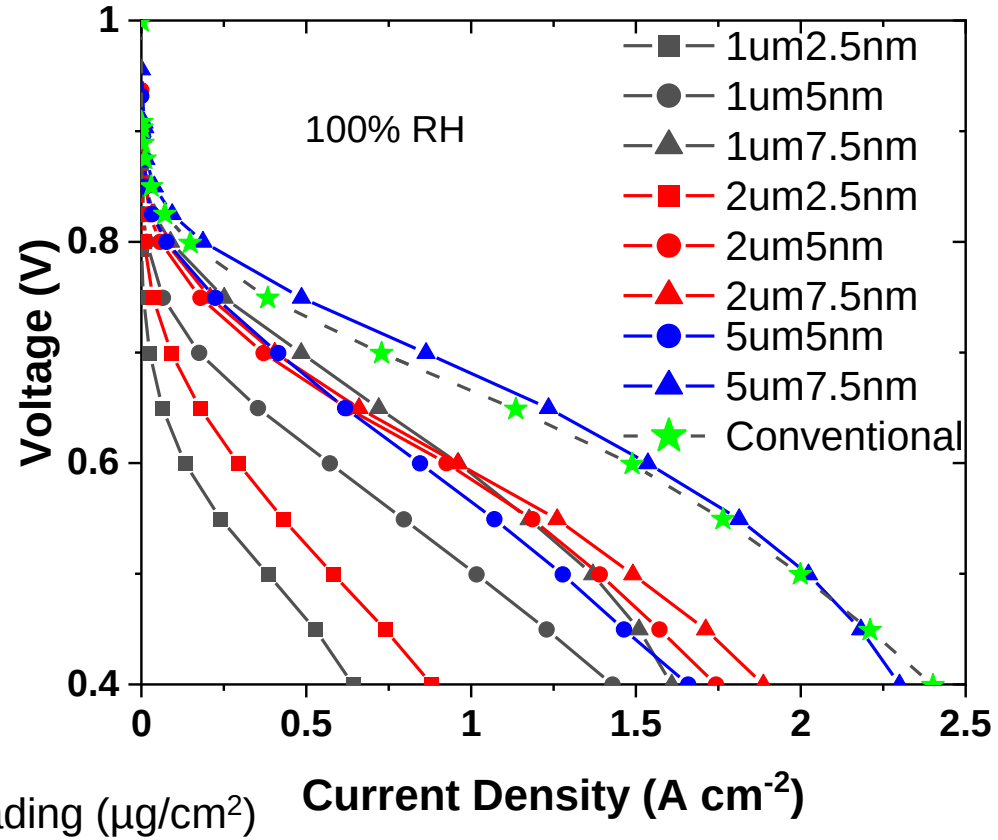


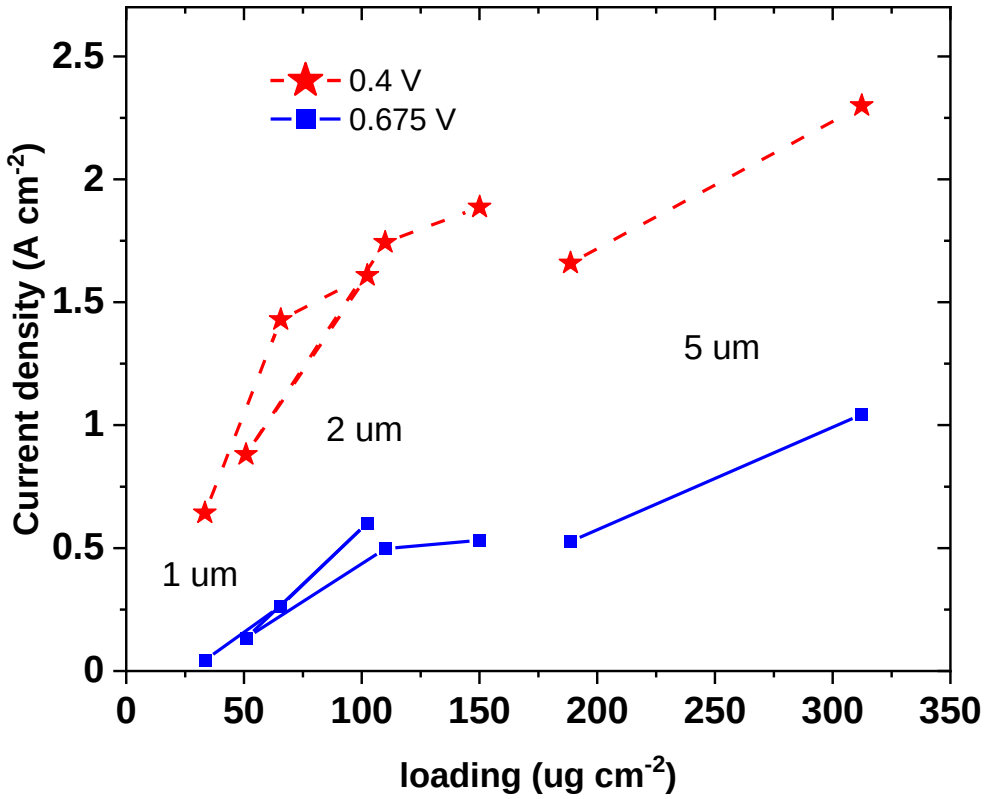




- Higher mass activity and smaller RO2 explain better performance of 5µm7.5nm
- Conventional CCM: 0.18A/mg$_{Pt}$ and 65 m2/g$_{Pt}$
- 5µm7.5nm has a lowest RO2

Co-Axial Nanowire Electrodes





Pt loading (μg/cm²)

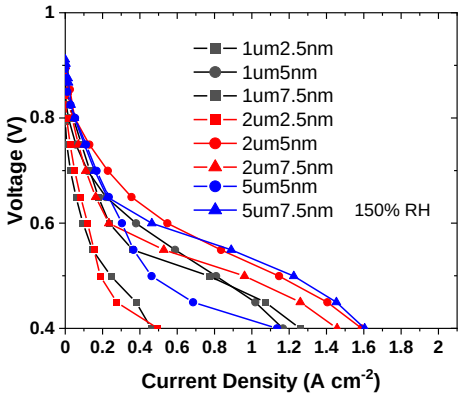
Pt thickness \ Height	1 μm	2 μm	5 μm
2.5 nm	33.4	50.9	61.3
5 nm	65.7	110.0	188.7
7.5 nm	102.5	150.1	312.4

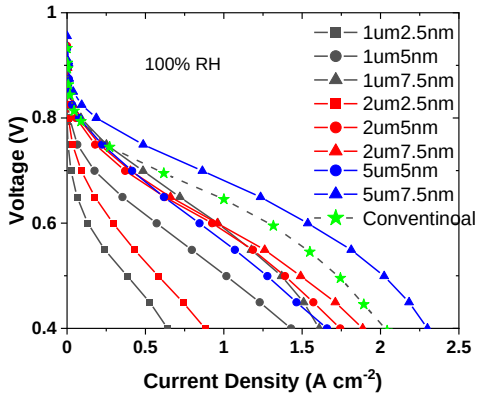
- Good performance was achieved by CANEs (5μm 7.5nm)
- However, loading is not the only reason for good performance
  - Similar performance observed from CANEs with different loadings

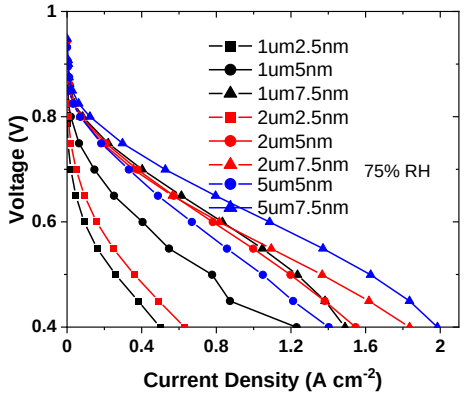
25 μm membrane; H_2/Air; Cell temperature: 80 °C; 150 kPa **Conventional CCM** loading: TEC10E40E 100 μg/cm²

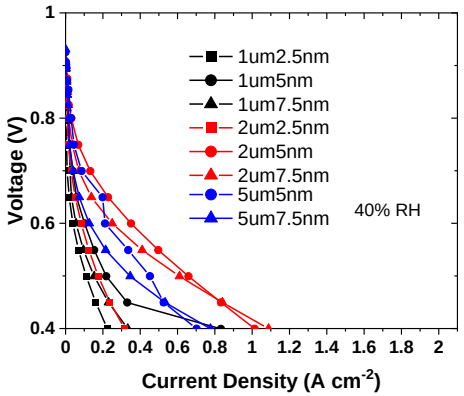
·Backup

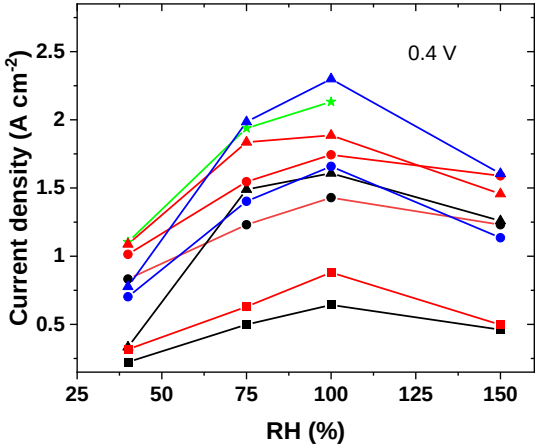
Co-Axial Nanowire Electrodes: Different RHs

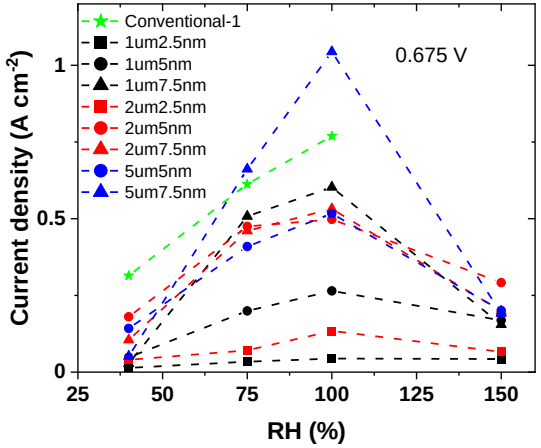








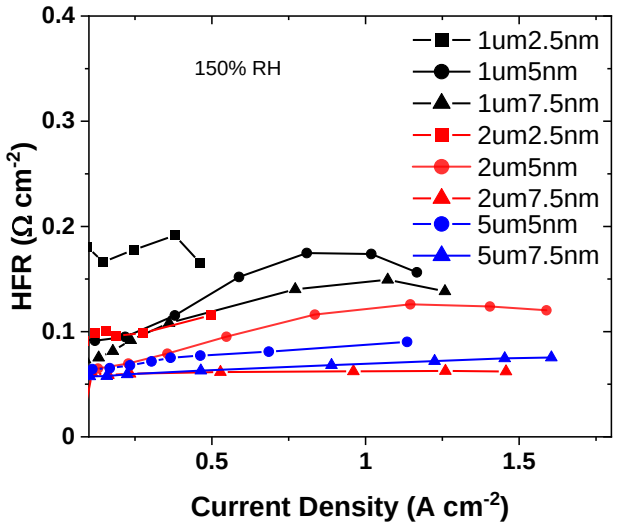


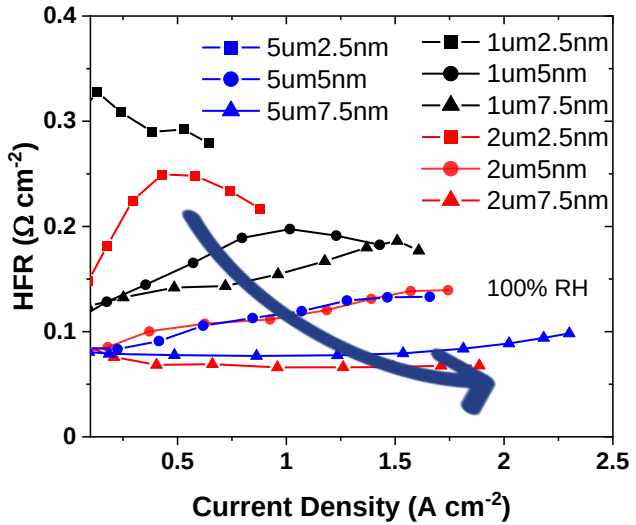


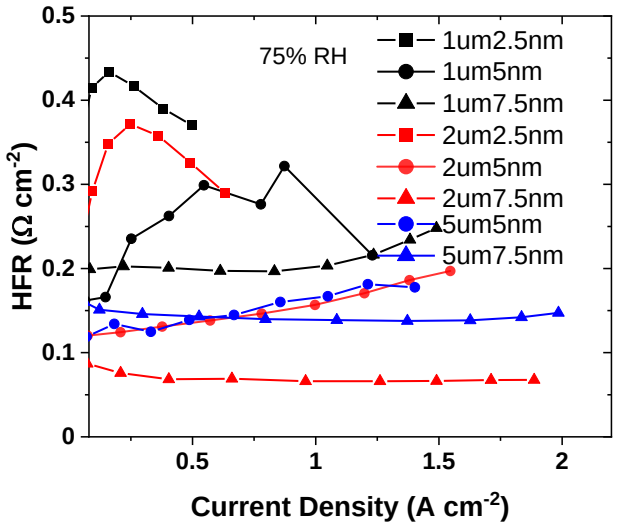
- 5µm7.5nm provide best performance at 100% RH
- Performance of 5µm7.5nm is reduced at high and low RH (150% and 40%)
- CANE electrodes are sensitive to RH

25 µm membrane; H_2/Air; Cell temperature: 80 °C; 150 kPa **Conventional CCM** loading: TEC10E40E 100 µg/cm^2

Co-Axial Nanowire Electrodes: Different RHs

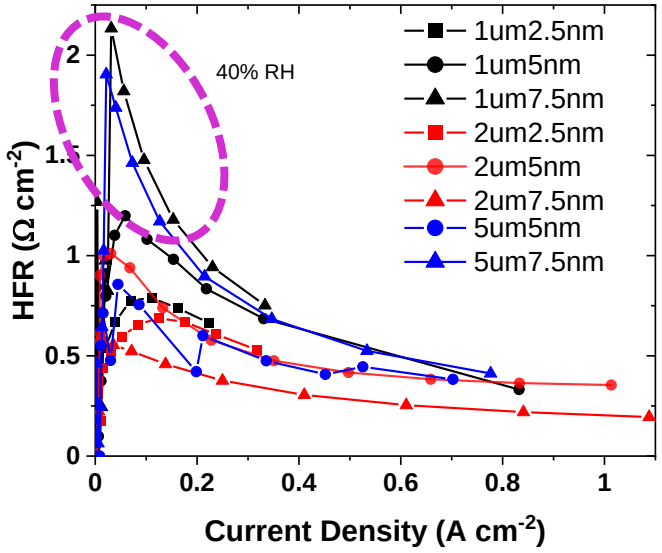






Low	High	Pt thickness
Low	High	Electron conductivity
High	Low	Proton conductivity

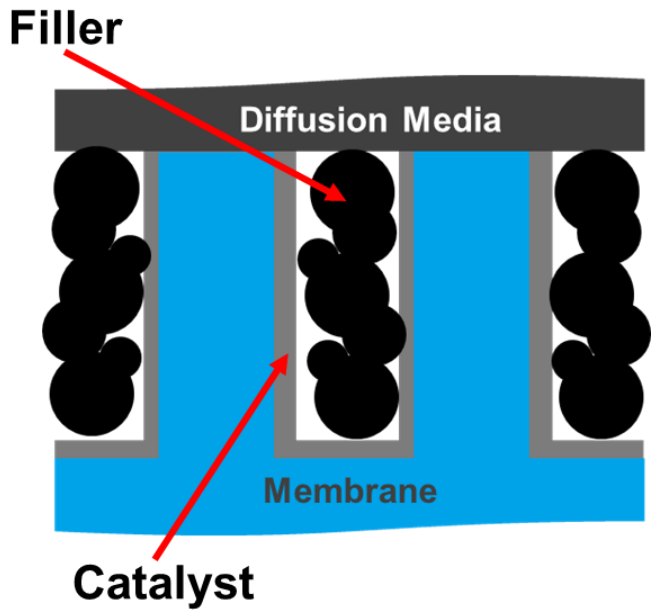
- Thicker Pt layer leads to higher HFR at 40% RH, due to the smaller water permeability and higher protonic resistance.



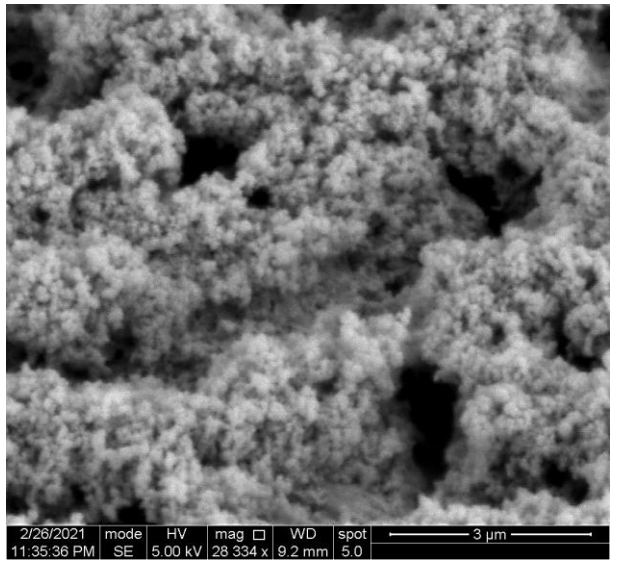
25 µm membrane; H_2/Air; Cell temperature: 80 °C; 150 kPa **Conventional CCM** loading: TEC10E40E 100 µg/cm²

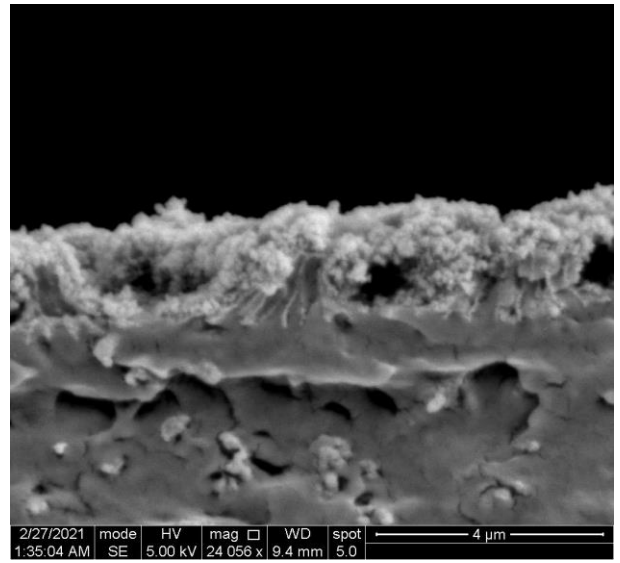
CANE: C-filler

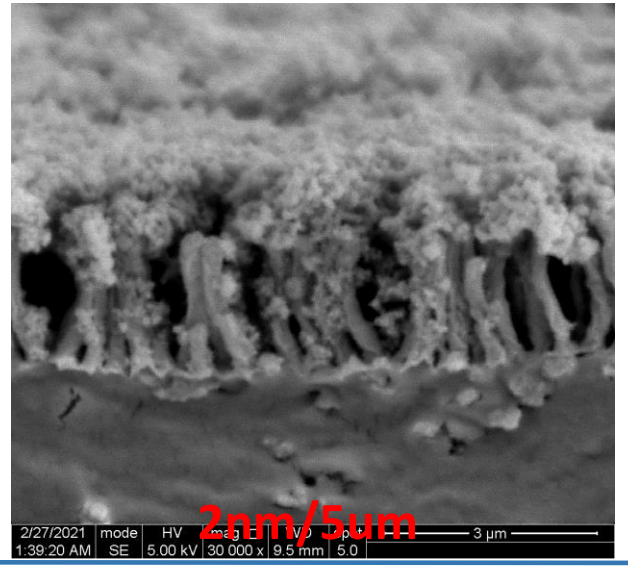
- Sonication procedures: 2min probe + 3h bath
- XC-72 ink with 0.1 I/C
- Carbon concertation: 0.05%
- Catalysts cover pillars



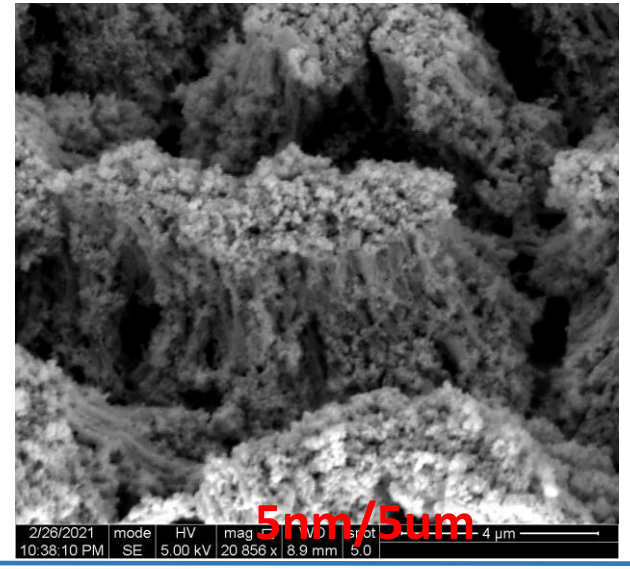
2nm/2.5um







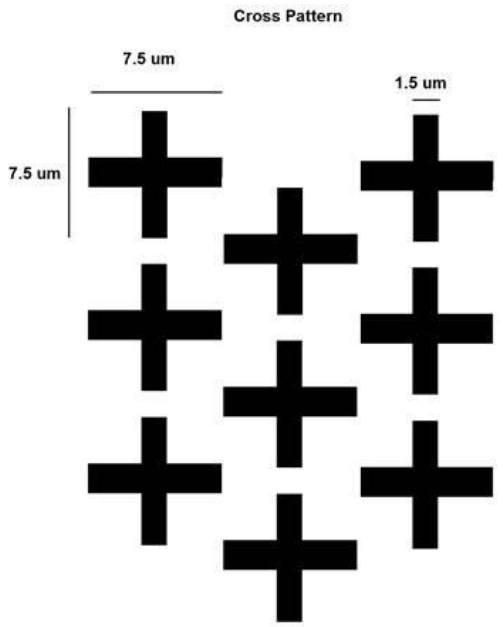
2nm/5um

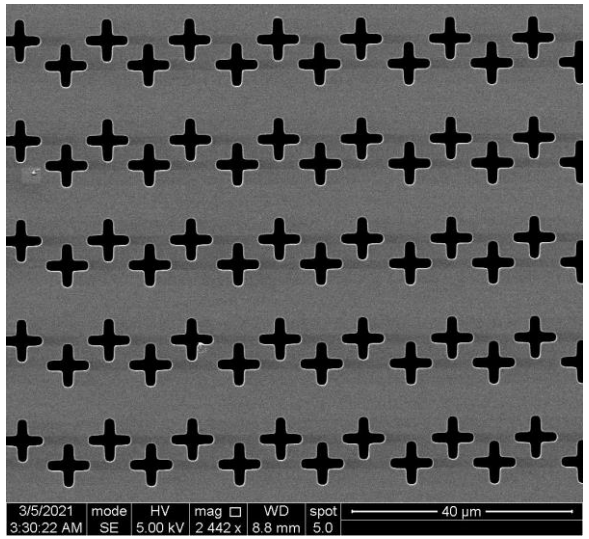


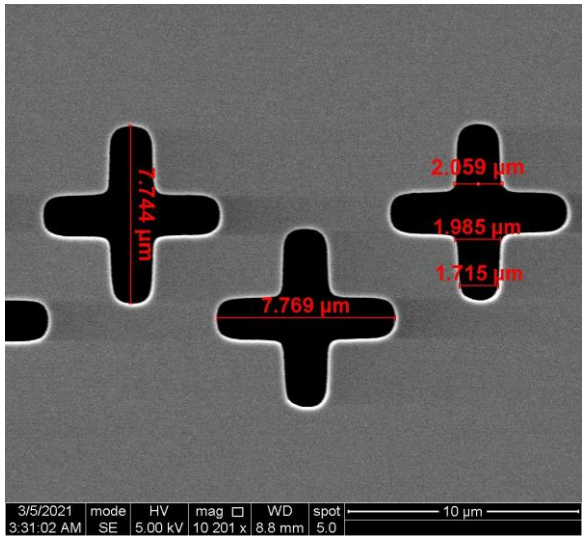
5nm/5um

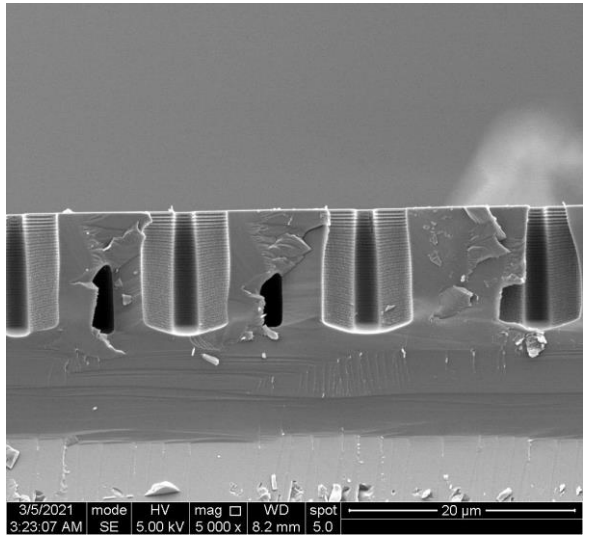
Cross-shape pillar

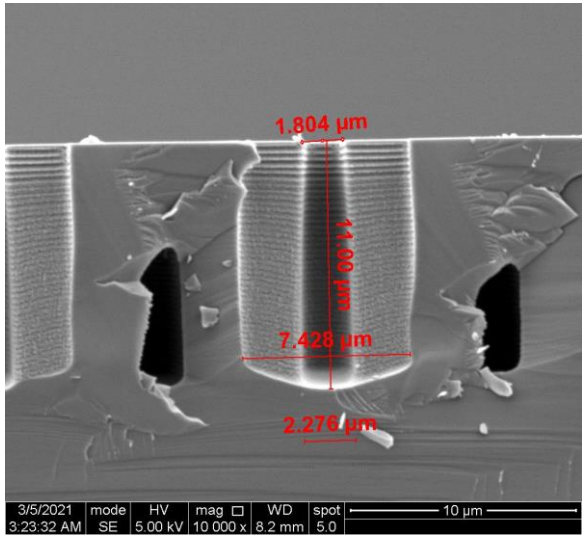
- Enhancing the strength of the pillar
- Preventing pillar collaps



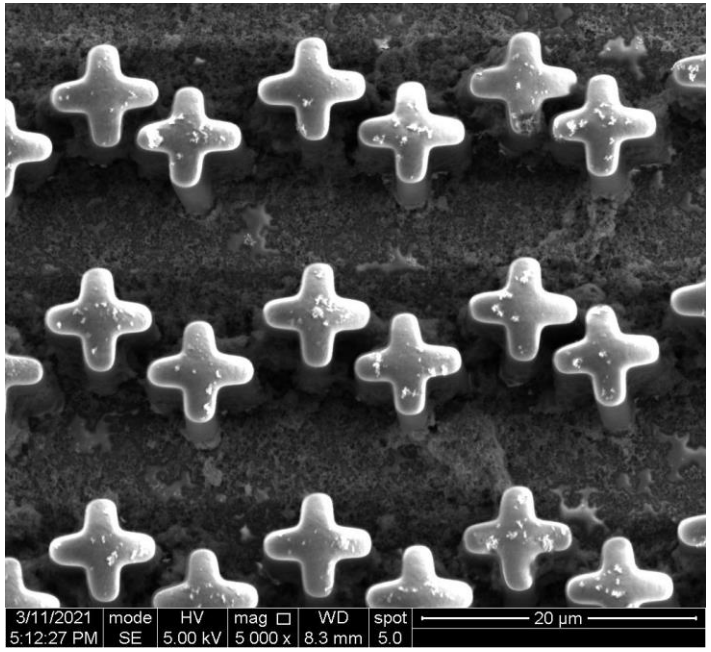


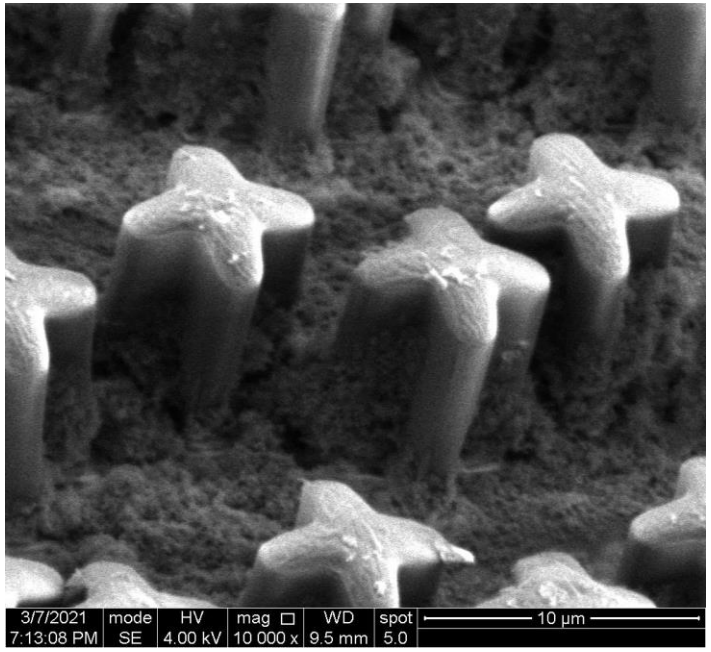


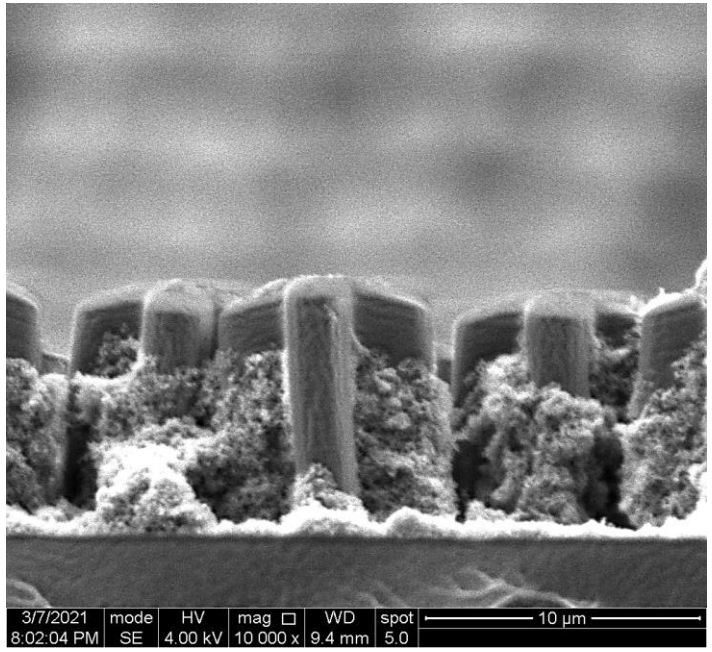




Cross-shape pillar







23 ug/cm^2 loading

45 ug/cm^2 loading

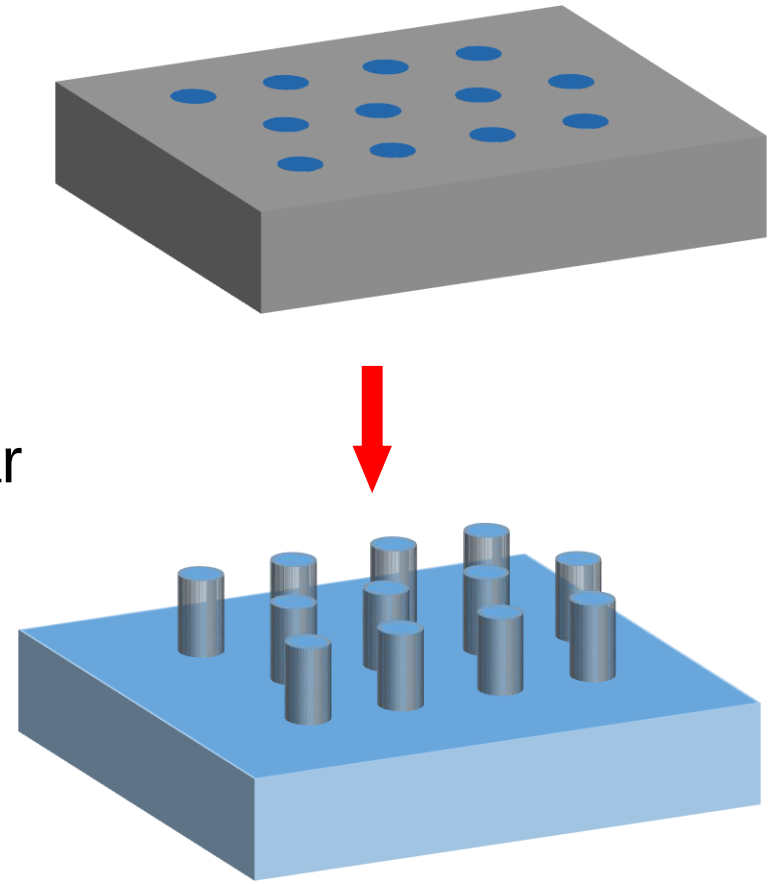
- Different loadings
- No severe collapse is found.
- Catalysts were deposited on the surface

Inverse Array Electrode

Reasoning for inverse pillars:

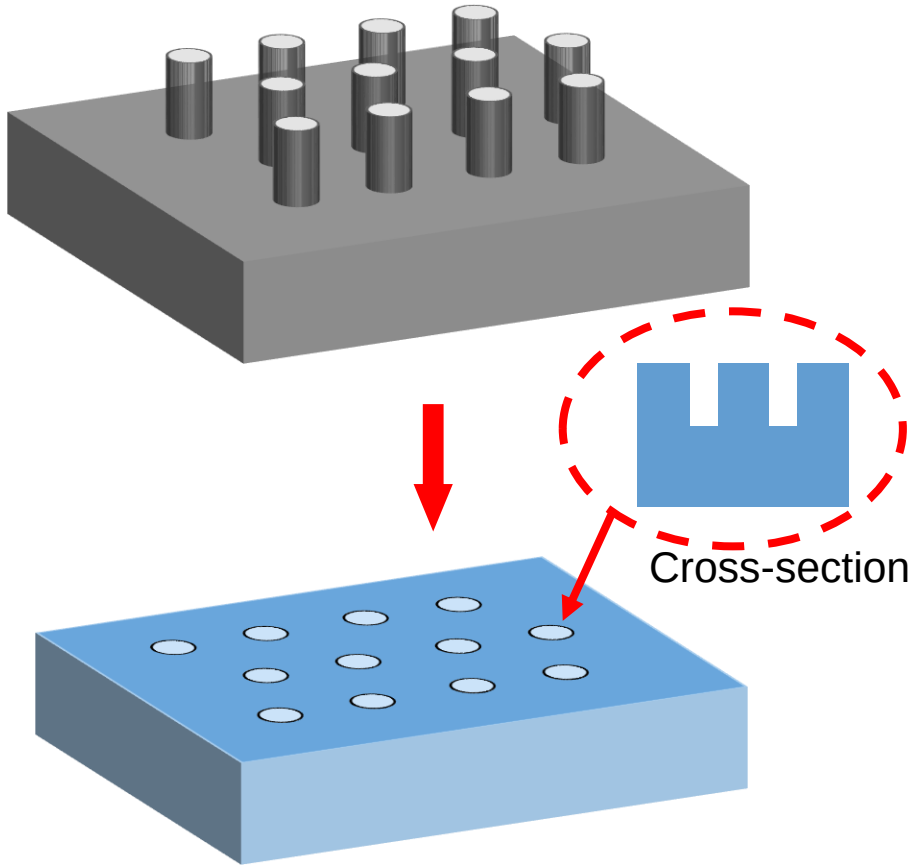
- Better mechanical strength
- Prevention of pillar collapse

Regular Si template with arrayed holes



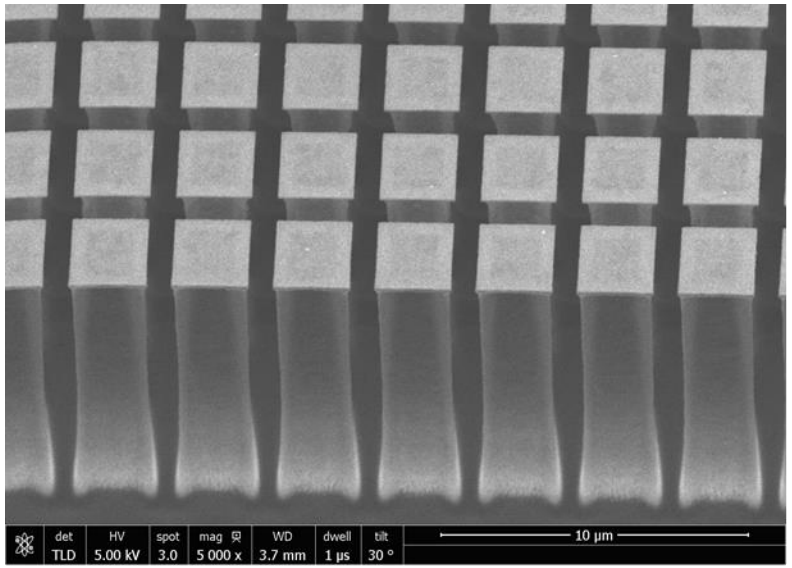
Patterned membrane with pillars

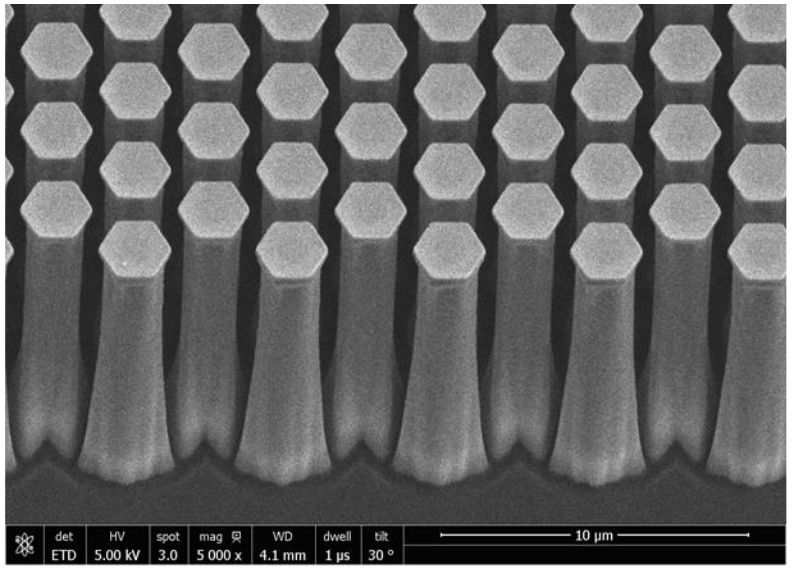
Inverse Si template with arrayed pillars

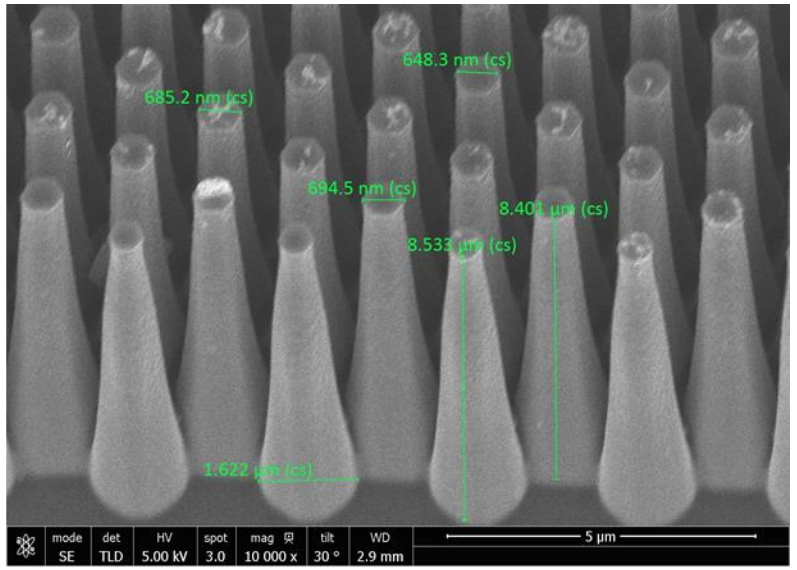


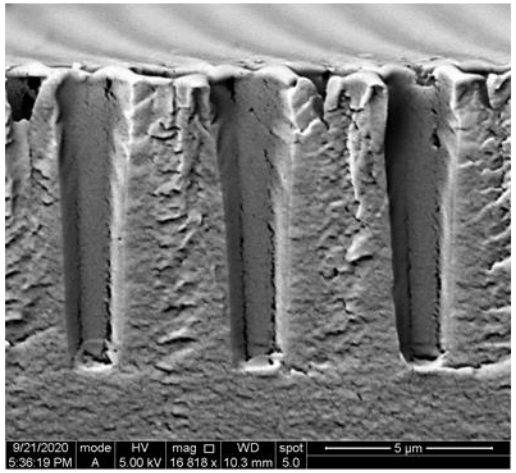
Patterned membrane with inverse pillars

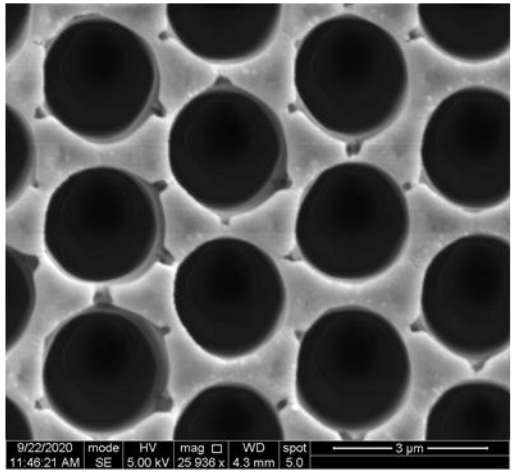
Inverse Array Electrode

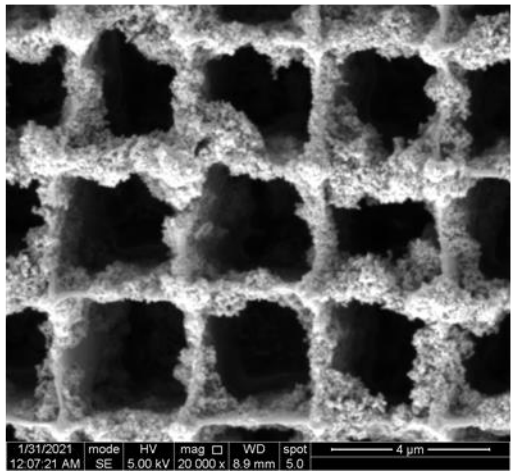




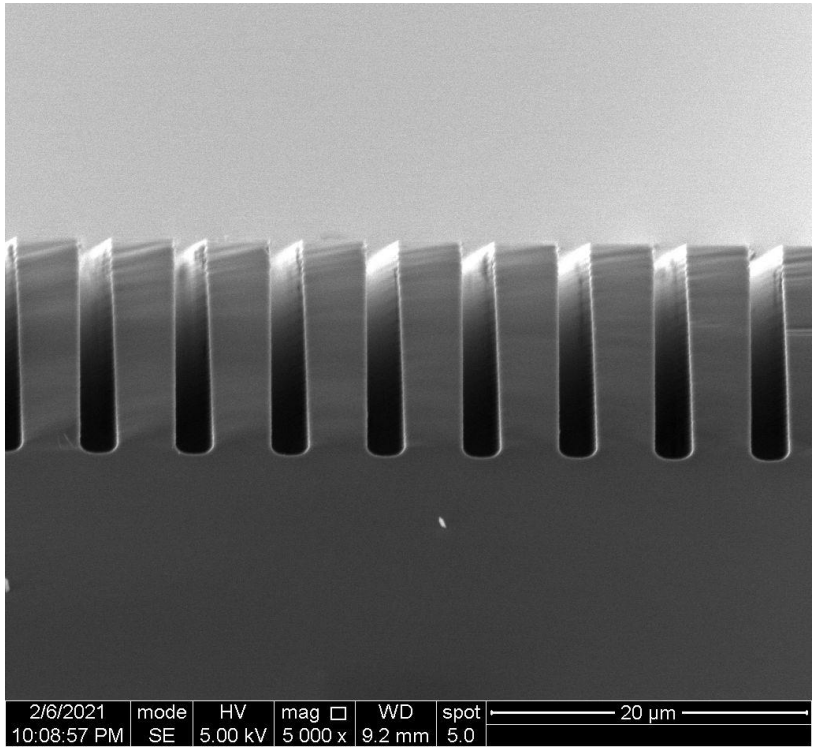


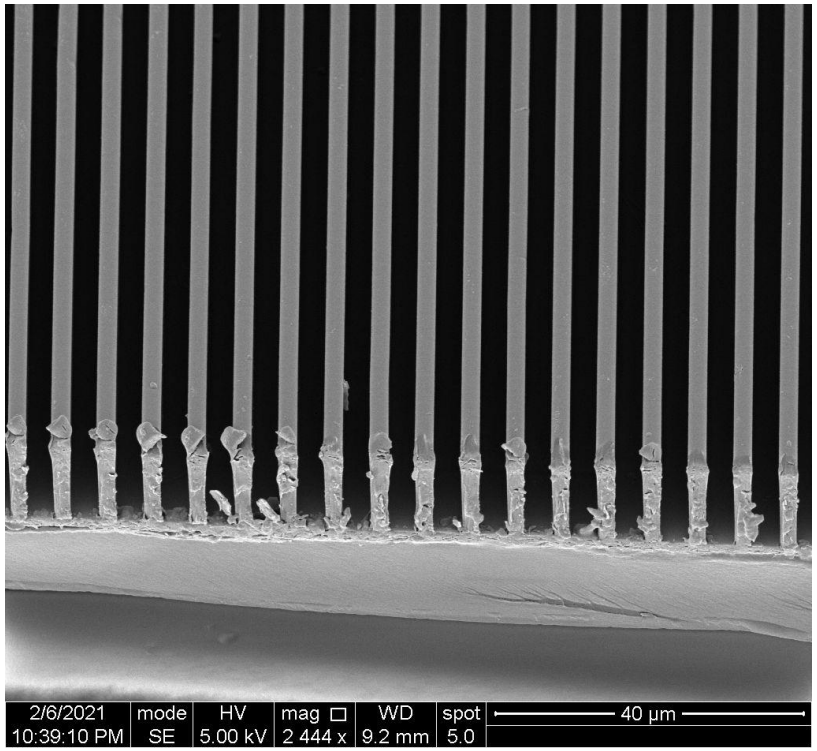






Ridge





Si template with ridge

Nafion ridge

- Ridge width: 4.1 um/3.7 um
- Gap width: 2.0um/2.5um
- Ridge height: 13.4 um